DETERMINATION OF POLYCYCLIC AROMATIC COMPOUNDS CONTAINING BOTH SULFUR AND NITROGEN HETEROATOMS IN COAL-DERIVED PRODUCTS

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Coal-derived products are extremely complex mixtures of organic chemicals, the majority of which are polycyclic aromatic compounds (PAC). While the polycyclic aromatic hydrocarbons (PAH) comprise the largest chemical class fraction of most coal products, there are substantial amounts of nitrogen-, sulfur-, and oxygen-containing PAC. After fractionation of the nitrogen-containing PAC fraction, it was found that the amino polycyclic aromatic hydrocarbons (APAH), which are present in low concentrations (usually less than 1%), were responsible for the major part of the mutagenicity (1-4). The nitrogen heterocycles were generally much less mutagenic than the APAH. This result has prompted the investigation of other possible trace components in coal products, particularly the PAC that contain two heteroatoms, that may be responsible for some of the observed biological activity.

In this paper, the analysis of a solvent-refined coal liquid and a coal tar for PAC which contain both nitrogen and sulfur heteroatoms is described. Capillary column gas chromatography with sulfur-selective flame photometric detection and mass spectrometry were used to identify several new compounds which were previously unreported. Pure reference compounds were also synthesized and tested for genotoxicity.

EXPERIMENTAL

The solvent-refined coal heavy distillate (SRC II HD: 260-450°C boiling point range) was obtained from the Fort Lewis, Washington, pilot plant (operated by the Pittsburgh & Midway Coal Mining Co.). The coal tar was obtained from S.A. Wise (National Bureau of Standards, Washington, D.C.). The four aminodibenzothiophene isomers and azathiophenic compounds used in this study were not commercially available and, therefore, had to be synthesized in our own laboratories. The synthetic procedures are reported elsewhere (5,6).

The SRC II HD material and coal tar were fractionated into chemical classes by adsorption chromatography on neutral alumina and silicic acid according to the procedure of Later et al. (7). The third fraction (A-3) which was composed of the nitrogen-containing PAC, the second silicic acid fraction (S-2) which was composed of the APAH, and the third silicic acid fraction (S-3) which was composed of the tertiary nitrogen-containing PAC were analyzed in this study. Acid extraction with H_2SO_4, and derivatization with pentafluoropropionic anhydride (PFPA) were previously described (8).

A Hewlett-Packard Model 5880 gas chromatograph equipped with a sulfur-selective flame photometric detector (FPD), and operated in the splitless injection mode was used to obtain chromatographic retention data. Hydrogen was used as the carrier gas at a linear velocity of 100 cm s^{-1}. The capillary column used in this study was prepared by coating a 20 m x 0.31 mm i.d. length of fused silica tubing (Hewlett-Packard, Avondale, PA) with a 25% biphenyl polymethylsiloxane stationary phase (0.25 µm film thickness) (9). A Hewlett-Packard Model 5982A GC-MS system was used to obtain mass spectral confirmation of identified compounds. The same chromatographic column was used as for gas chromatography, and the mass spectrometer was operated in the electron impact mode at 70 eV electron energy. The Ames mutagenicity assay was performed as described by Ames et al. (10) with minor modifications.

RESULTS AND DISCUSSION

The chromatogram of the SRC II HD A-3 fraction on the 25% biphenyl methylpolysiloxane stationary phase is shown in Figure 1. Retention times were compared with the newly synthesized standard samples, and the 1- to 4-aminodibenzothiophenes and various azathiophenic compounds were identified. Several small peaks (most likely sulfur-containing secondary nitrogen heterocycles) were eliminated after acid extraction of the fraction. A modification of the method described by Later et al. (11) was used to distinguish the sulfur/tertiary nitrogen-containing PAH and sulfur/amino-containing PAH. Comparison of the chromatogram of the PFP derivatives with Figure 1 showed that some of the peaks shifted in retention time after derivatization. Retention times for the PFP amide derivatives decreased because the polar amino groups were blocked by the PFP groups, causing less dipole/induced dipole interactions with the polarizable biphenyl stationary phase. Identification of the four aminodibenzothiophene isomers was confirmed by comparing the retention times of the PFP-derivatized standards with the retention times of the shifted peaks in the chromatogram of the PFP-derivatized A-3 fraction. A chromatogram of the S-2 APAH fraction of the SRC II HD showed only aminodibenzothiophenes and alkylated aminodibenzothiophenes.

The chromatogram of the coal tar A-3 fraction on the 25% biphenyl methylpolysiloxane stationary phase is shown in Figure 2. Retention times of compounds in both the A-3 and S-3 fractions were compared with the reference samples, and 3 isomers of the azabenzothiophenes and all isomers of the azadibenzothiophenes were identified. In contrast to the SRC II HD, azathiophenic compounds were major components and aminodibenzothiophenes were not found.

Further confirmation of peak identities was obtained by GC-MS analysis. Table 1 lists the relative retention times of the PAC containing both sulfur and nitrogen identified in this study and the result of semi-quantitation of several of these compounds in the samples.

Tertiary nitrogen heterocycles are more thermally stable than amino-containing PAC, and are major nitrogen-containing PAC in coal-derived products (12). Azathiophenic compounds were tentatively identified in an anthracene oil and coal tar using GC-MS by Burchill et al.(12,13). However, the aminodibenzothiophenes were the major nitrogen/sulfur-containing heterocycles in this coal liquid, while the azathiophenic compounds were the major ones in the coal tar. The difference between the two coal-derived products apparently relates to the reaction conditions. In the SRC II process, hydrogen was used
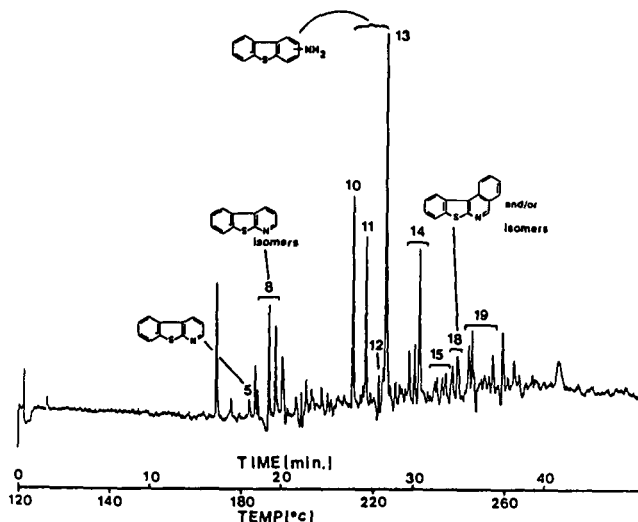
Figure 1. FPD chromatogram of the SRC II HD A-3 fraction on a 25% biphenyl polysiloxane stationary phase. Conditions: temperature program from 120°C to 265°C at 4°C min⁻¹, after an initial 2-min isothermal period; hydrogen carrier gas at 100 cm s⁻¹. Peak assignments are listed in Table 1.
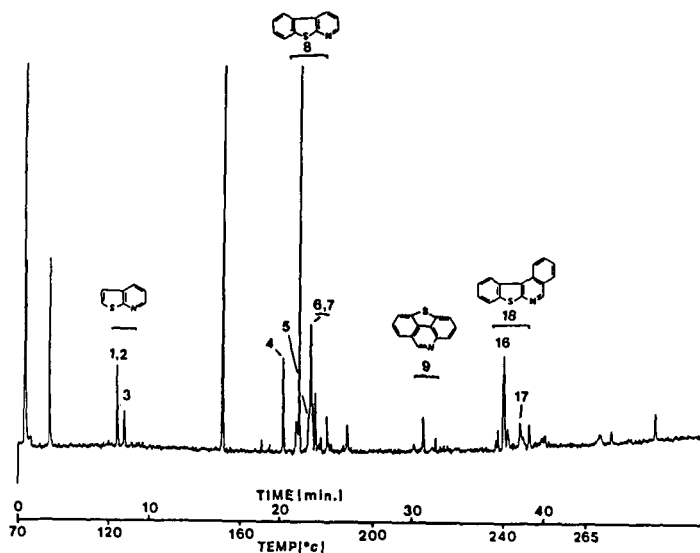

Figure 2. FPD chromatogram of the coal tar A-3 fraction on a 25% biphenyl polysiloxane stationary phase. Conditions: temperature program from 70 °C to 120°C at 10°C min⁻¹, then from 120°C to 265°C at 4°C min⁻¹, after an initial 2-min isothermal period; hydrogen carrier gas at 100 cm s⁻¹. Peak assignments are listed in Table 1.

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Table 1. Relative retention times and semi-quantitation (selected examples) of PAC containing both sulfur and nitrogen in an SRC II heavy distillate coal liquid and a coal tar.

Peak No.	Compound[a]	Relative Retention Time[b]	Concentration[c] (μg/g)	
			SRC II HD	Coal Tar
1	4-azabenzothiophene	0.361		
3	6-azabenzothiophene	0.380		0.18
2	7-azabenzothiophene	0.361		
4	1-azadibenzothiophene	0.956		1.7
6	2-azadibenzothiophene	1.05		
7	3-azadibenzothiophene	1.05		
5	4-azadibenzothiophene	1.04		
8	azadibenzothiophene isomers	-		
-	1-azanaphtho[2,1-b]thiophene	0.979		
9	azaphenanthro[4,5-b,c,d]thiophene isomers	-		
11	1-aminodibenzothiophene	1.47	0.32	
12	2-aminodibenzothiophene	1.52	0.11	
13	3-aminodibenzothiophene	1.54	2.5	
10	4-aminodibenzothiophene	1.43	0.33	
14	C_1 aminodibenzothiophene	-		
15	C_2 aminodibenzothiophene	-		
16	3-azaphenanthro[9,10-b]thiophene	1.74		
-	3-azaphenanthro[2,1-b]thiophene	1.78		
17	3-azaphenanthro[4,3-b]thiophene	1.80		
-	1-azaphenanthro[1,2-b]thiophene	-[d]		
-	5-azabenzo[b]naphtho[1,2-d]thiophene	-[d]		
18	azabenzonaphthothiophene isomers	-		
19	C_1 azabenzonaphthothiophene isomers	-		

[a]Compounds which are not numbered were not found in these coal-derived products.
[b]Retention relative to naphto[2,3-b]thiophene.
[c]Approximate concentration in μg/g in the crude SRC II heavy distillate and the coal tar.
[d]Compound did not elute under the chromatographic conditions used.

in the reaction, and metals contained in the recycle oil were utilized as catalysts (14). Therefore, aminodibenzothiophenes seem to be more abundant than azathiophenic compounds in the coal liquid because of hydrogenation in the process. On the other hand, sulfur/tertiary nitrogen-containing PAC were thought to be major components in the high-temperature treated coal tar sample. Similarly, the easily desulfurized sulfur heterocycles such as naphtho[2,3-b]thiophene, 4- and 5-ring sulfur heterocycles derived from naphtho[2,3-b]thiophene were not found in SRC II sample, while these sulfur heterocycles were present in the same coal tar as reported elsewhere (15).

The mutagenicities of all isomers of the aminodibenzothiophenes and the

Table 2. Ames mutagenicity of the aminodibenzothiophenes and azadibenzo-
thiophenes.

Compound	rev/μg[a]	R^2
1-aminodibenzothiophene		
0% S9[b]	c	--
4% S9[d]	2.36	0.96
2-aminodibenzothiophene		
0% S9[b]	9.07	0.98
4% S9[e]	1.94×10^4	0.97
3-aminodibenzothiophene		
0% S9[b]	4.74	0.90
4% S9[f]	3.43×10^3	0.97
4-aminodibenzothiophene		
0% S9[b]	c	--
4% S9[d]	c	--
1-azadibenzothiophene		
4% S9[g]	c	--
2-azadibenzothiophene		
4% S9[h]	c	--
3-azadibenzothiophene		
4% S9[h]	c	--
4-azadibenzothiophene		
4% S9[g]	c	--

[a]Linear response region used to calculate dose response by
linear regression curve fitting.
[b]Solvent control value (0% S9): 21+4
[c]Response < 2X solvent control values
[d]Solvent control value (4% S9): 38+5
[e]Solvent control value (4% S9): 29+4
[f]Solvent control value (4% S9): 31+4
[g]Solvent control value (4% S9): 38+2
[h]Solvent control value (4% S9): 46+6

azadibenzothiophenes are listed in Table 2. The 2- and 3-aminodibenzothio-
phenes are strongly mutagenic, and their average mutagenic response was ten to
one hundred times greater than the average response of benzo[a]pyrene (200-300
revertants/plate at 4 μg and 4% S9) (16). All isomers of the azadibenzo-
thiophenes were inactive. A comparison of the structures of aminodibenzo-
thiophenes to the aminophenanthrenes reveals a geometric similarity between
them. The 2-, 3-, and 9-aminophenanthrenes demonstrated the highest muta-
genicity of the aminophenanthrene isomers (17). The 3-aminophenanthrene
isomer had the strongest mutagenicity (30,300 rev/μg average response), and
this structure is analogous to 2-aminodibenzothiophene which is the most
active of the aminodibenzothiophene isomers.

ACKNOWLEDGMENT

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